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Equation of state of additive hard-disk fluid mixtures: A critical analysis of two recent proposals

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A detailed analysis of two different theoretical equations of state for a binary mixture of additive hard disks [C. Barrio and J. R. Solana, Phys. Rev. E **63**, 011201 (2001); A. Santos, S. B. Yuste and M. López de Haro, Mol. Phys. **96**, 1 (1999)], including their comparison with Monte Carlo results, is carried out. It is found that both proposals, which require the equation of state of the single component system as input, lead to comparable accuracy when the same input is used in both, but the one advocated by Santos *et al.* is simpler and complies with the exact limit in which the small disks are point particles.

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I. INTRODUCTION

Despite being in principle a simpler system, hard-disk fluid mixtures have received much less attention in the literature than fluid mixtures of hard spheres. This may well be tied to the fact that up to now no analytical solution to the Percus–Yevick equation has been found for even dimensionality. In any case, what this has meant is that fewer results are available for fluid mixtures of hard disks than for hard-sphere mixtures. In particular, a very scarce number of proposals for the equation of state (EOS) of these mixtures has been made [1, 2, 3, 4, 5], although the trend seems to be reversing recently, and even fewer simulations have been performed to assess the value of such proposals. In a recent paper, Barrio and Solana [5] proposed an EOS for a binary mixture of additive hard disks. Such an equation reproduces the (known) exact second and third virial coefficients of the mixture and may be expressed in terms of the EOS of a single component system. They also performed Monte Carlo simulations and found that their recipe was very accurate provided an also very accurate EOS for the single component system (in their case it was the EOS proposed by Woodcock [6]) was taken as input. The comparison with other EOS for the mixture available in the literature indicated that their proposal does the best job with respect to the Monte Carlo data. Among these other EOS for the binary mixture considered in Ref. [5], only the one introduced by Santos *et al.* a few years ago [3] also shares with Barrio and Solana's EOS the fact that it may be expressed in terms of the EOS for a single component system. The aim of the present paper is to present a detailed analysis of these two different equations of state since the comparison made in Ref. [5] may be misleading in that it was not performed by taking the *same* EOS for the single component system in both proposals. A preliminary report of this work can be found in Ref. [7].

In order to carry out the analysis, the paper is organized as follows. In Sec. II we recall the two different formulations for the EOS of a binary mixture of additive hard disks in a unified notation as well as provide the explicit (approximate) expressions for the EOS of the single component system that will be used in the actual calculations. This is followed in Sec. III by a discussion of the results and some concluding remarks.

II. THE EQUATION OF STATE OF A BINARY MIXTURE OF ADDITIVE HARD DISKS

Let us consider a binary mixture of additive hard disks of diameters σ_1 and σ_2. The total number density is ρ, the mole fractions are x_1 and $x_2 = 1 - x_1$, and the packing fraction is $\eta = \frac{\pi}{4}\rho\langle\sigma^2\rangle$, where $\langle\sigma^n\rangle \equiv \sum_i x_i\sigma_i^n$. Let $Z = p/\rho k_B T$ denote the compressibility factor, p being the pressure, T the absolute temperature and k_B the Boltzmann constant. Then, Barrio and Solana's EOS for a binary mixture of hard disks, $Z_{\mathrm{m}}^{\mathrm{BS}}(\eta)$, may be written in terms of a given EOS for a single component system, $Z_{\mathrm{s}}(\eta)$, as

$$Z_{\mathrm{m}}^{\mathrm{BS}}(\eta) = 1 + \frac{1}{2}(1+\beta\eta)(1+\xi)\left[Z_{\mathrm{s}}(\eta) - 1\right], \qquad (1)$$

where $\xi \equiv \langle\sigma\rangle^2/\langle\sigma^2\rangle$ and β is adjusted as to reproduce the exact third virial coefficient for the mixture B_3, namely

$$\beta = \frac{B_3}{(\pi/4)^2\langle\sigma^2\rangle^2(1+\xi)} - \frac{b_3}{2}. \qquad (2)$$

Here, $b_3 = 4(4/3 - \sqrt{3}/\pi)$ is the reduced third virial coefficient for the single component system and B_3 is

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given by [1]

$$B_3 = \frac{\pi}{3}\left(a_{11}x_1^3\sigma_1^4 + 3a_{12}x_1^2x_2\sigma_{12}^4 + 3a_{21}x_1x_2^2\sigma_{12}^4 + a_{22}x_2^3\sigma_2^4\right), \quad (3)$$

where

$$a_{ij} = \pi + 2\left(\sigma_i^2/\sigma_{ij}^2 - 1\right)\cos^{-1}(\sigma_i/2\sigma_{ij}) - \left(4\sigma_{ij}^2/\sigma_i^2 - 1\right)^{1/2}(1+\sigma_i^2/2\sigma_{ij}^2)\sigma_i^2/2\sigma_{ij}^2 \quad (4)$$

and $\sigma_{ij} = (\sigma_i + \sigma_j)/2$.

The EOS for the mixture, consistent with a given EOS for a single component system, introduced recently by Santos *et al.* reads [3]

$$Z_{\mathrm{m}}^{\mathrm{SYH}}(\eta) = (1-\xi)\frac{1}{1-\eta} + \xi Z_{\mathrm{s}}(\eta). \quad (5)$$

We stress the fact that Eq. (5) is simpler than Eq. (1) [which must be complemented with Eqs. (2)–(4)]. In addition, the structure of Eq. (5) is valid for any number of components, while Eq. (1) requires the third virial coefficient, which is known exactly only for *binary* mixtures. In order to proceed with a quantitative analysis of Eqs. (1) and (5), we have to specify $Z_{\mathrm{s}}(\eta)$. While many choices are available, we will restrict ourselves to the three following EOS of the single component system:

a) Woodcock's EOS [6]

$$Z_{\mathrm{s}}^{\mathrm{W}}(\eta) = \frac{1+3\eta/\eta_0}{1-\eta/\eta_0} + \sum_{n=2}^{6}\left(b_n\eta_0^{n-1} - 4\right)(\eta/\eta_0)^{n-1}, \quad (6)$$

where $\eta_0 = \left(\sqrt{3}/6\right)\pi$ is the value of the crystalline close-packing and the b_n ($n = 2, \ldots, 6$) are the (known) reduced virial coefficients [8].

b) The Levin approximant of Erpenbeck and Luban [9]

$$Z_{\mathrm{s}}^{\mathrm{EL}}(\eta) = \frac{\sum_{n=0}^{4} p_n\eta^n}{\sum_{n=0}^{5} q_n\eta^n}, \quad (7)$$

where $q_n = (-1)^n \binom{6}{n}(1-n/6)^5\, b_6/b_{6-n}$ and $p_n = \sum_{m=0}^{n} b_{n+1-m}q_m$.

c) The EOS proposed by Santos *et al.* [10, 11]

$$Z_{\mathrm{s}}^{\mathrm{SHY}}(\eta) = \left(1 - 2\eta + \frac{2\eta_0 - 1}{\eta_0^2}\eta^2\right)^{-1}. \quad (8)$$

The EOS (6) and (7) are more complex than the EOS (8) in the sense that they require the exact knowledge of the first six virial coefficients, while Eq. (8) is constructed by using the first two virial coefficients only and enforcing a pole at $\eta = \eta_0$. Despite its simplicity, however, Eq. (8) does a remarkably good job when compared with simulation data, although it is of course less accurate than the more sophisticated EOS (6) and (7) [10].

III. DISCUSSION

In Table I, we show the results of Eqs. (1) and (5) when Woodcock's EOS [6], Eq. (6), for the single component system is used as input in both equations, as well as the available MC data [5]. As seen in Table I, it is fair to say that both recipes are of comparable accuracy with respect to the Monte Carlo results, their difference being generally smaller than the error bars of the simulation data, although $Z_{\mathrm{m}}^{\mathrm{BS}}(\eta)$ performs slightly better than $Z_{\mathrm{m}}^{\mathrm{SYH}}(\eta)$. This may be fortuitous since if one takes for $Z_{\mathrm{s}}(\eta)$ in Eqs. (1) and (5) the Levin approximant [9], Eq. (7), (which is known to give the most accurate approximation to the single component compressibility factor [9, 10]) the apparent (slight) superiority of $Z_{\mathrm{m}}^{\mathrm{BS}}(\eta)$ is no longer there. For instance, the theoretical values of Table I corresponding to the packing fraction $\eta = 0.6$ are increased by about 0.03 when the Levin approximant rather than Woodcock's EOS is used as input, so that in this case the accuracy of $Z_{\mathrm{m}}^{\mathrm{SYH}}(\eta)$ is generally slightly better than that of $Z_{\mathrm{m}}^{\mathrm{BS}}(\eta)$. This is further illustrated in Figs. 1-3, where in order to enhance the differences we have plotted $Z_{\mathrm{m}}(\eta) - Z_{\mathrm{m}}^{\mathrm{BS(W)}}(\eta)$ versus η, $Z_{\mathrm{m}}^{\mathrm{BS(W)}}(\eta)$ indicating the use of Eq. (1) taking for $Z_{\mathrm{s}}(\eta)$ the EOS by Woodcock. The figures show that, in general, the differences between the EOS (1) and the EOS (5), taking of course the same Z_{s} as input, are smaller than or of the order of the error bars of the simulation data. As expected, a better agreement with the simulation data is obtained when either of the more accurate EOS (6) or (7) is used as input instead of the much simpler EOS (8). It is interesting to remark that the best agreement at the two largest densities, $\eta = 0.55$ and $\eta = 0.6$, corresponds to the use of the Levin approximant for Z_{s}.

Let us try to understand why both EOS for the mixture give practically equivalent results when the same input is used in both. First, it may be shown that $Z_{\mathrm{m}}^{\mathrm{SYH}}(\eta)$, while not reproducing the exact third virial coefficient B_3, yields a very good estimate of it [12], namely $B_3 \simeq [1 + (b_3 - 1)\xi]\,(\pi/4)^2\langle\sigma^2\rangle^2$. If we replace that estimate into Eq. (2), we get

$$\beta \simeq \frac{1-\xi}{1+\xi}\left(1 - \frac{b_3}{2}\right). \quad (9)$$

By using this estimate in Barrio and Solana's EOS, Eq. (1), we have

$$Z_{\mathrm{m}}^{\mathrm{BS}}(\eta) - Z_{\mathrm{m}}^{\mathrm{SYH}}(\eta) \simeq (1-\xi)\,\Delta(\eta), \quad (10)$$

where

$$\Delta(\eta) \equiv \frac{1}{2}\left[1 - \left(\frac{b_3}{2} - 1\right)\eta\right][Z_{\mathrm{s}}(\eta) - 1] - \frac{\eta}{1-\eta}. \quad (11)$$

According to the approximation involved in Eq. (10), the difference $Z_{\mathrm{m}}^{\mathrm{BS}}(\eta) - Z_{\mathrm{m}}^{\mathrm{SYH}}(\eta)$ is small if the asymmetry of the mixture is small ($\xi \lesssim 1$) and/or $\Delta(\eta)$ is small. The function $\Delta(\eta)$ is plotted in Fig. 4 for the

TABLE I: Compressibility factor for different binary mixtures of hard disks as obtained from Monte Carlo simulations, from Eq. (1), and from Eq. (5). In the two latter, Woodcock's equation of state for the single component system is used.

		$x_1 = 0.25$			$x_1 = 0.50$			$x_1 = 0.75$		
σ_2/σ_1	η	MC[a]	Eq. (1)	Eq. (5)	MC[a]	Eq. (1)	Eq. (5)	MC[a]	Eq. (1)	Eq. (5)
2/3	0.20	1.559(6)	1.559	1.559	1.561(5)	1.558	1.558	1.565(4)	1.563	1.563
	0.30	2.036(8)	2.040	2.040	2.043(8)	2.039	2.039	2.051(8)	2.048	2.048
	0.40	2.79(1)	2.79	2.79	2.79(1)	2.78	2.78	2.80(1)	2.80	2.80
	0.45	3.31(1)	3.32	3.32	3.31(2)	3.32	3.32	3.33(1)	3.34	3.34
	0.50	4.02(2)	4.02	4.02	4.02(1)	4.02	4.02	4.04(2)	4.05	4.05
	0.55	4.98(2)	4.97	4.97	4.98(2)	4.96	4.96	5.03(2)	5.00	5.00
	0.60	6.31(2)	6.29	6.28	6.30(1)	6.28	6.27	6.36(3)	6.33	6.33
1/2	0.20	1.534(6)	1.536	1.536	1.540(6)	1.538	1.538	1.556(7)	1.552	1.552
	0.30	1.998(7)	1.995	1.995	2.008(7)	2.000	2.000	2.039(8)	2.027	2.026
	0.40	2.72(1)	2.70	2.70	2.71(1)	2.71	2.71	2.77(1)	2.76	2.76
	0.45	3.20(2)	3.21	3.21	3.22(2)	3.22	3.22	3.29(2)	3.29	3.29
	0.50	3.88(1)	3.88	3.87	3.90(2)	3.89	3.89	3.98(2)	3.98	3.98
	0.55	4.79(2)	4.77	4.76	4.81(2)	4.80	4.78	4.93(2)	4.91	4.90
	0.60	6.03(3)	6.02	6.00	6.04(2)	6.05	6.03	6.22(3)	6.21	6.20
1/3	0.20	1.491(6)	1.490	1.490	1.510(8)	1.506	1.506	1.538(9)	1.536	1.536
	0.30	1.907(8)	1.905	1.904	1.940(8)	1.937	1.936	2.004(9)	1.996	1.995
	0.40	2.55(1)	2.54	2.54	2.59(1)	2.60	2.60	2.71(1)	2.71	2.70
	0.45	2.99(2)	3.00	2.99	3.07(1)	3.07	3.06	3.20(2)	3.21	3.21
	0.50	3.60(2)	3.59	3.57	3.69(2)	3.69	3.68	3.89(2)	3.88	3.87
	0.55	4.39(3)	4.39	4.36	4.52(2)	4.52	4.50	4.79(2)	4.78	4.76
	0.60		5.49	5.44	5.66(6)	5.68	5.64	6.06(1)	6.03	6.00

[a]Ref. [5]

cases where $Z_\mathrm{s}(\eta)$ is given by Woodcock's EOS, by the Levin approximant, and by the SHY EOS. In all instances it is practically zero up to $\eta \approx 0.2$ but then it grows rapidly. The most disparate mixture considered in Barrio and Solana's simulations corresponds to $x_1 = 0.25$, $\alpha \equiv \sigma_2/\sigma_1 = 1/3$, which yields $\xi = 0.75$. This explains the fact that $Z_\mathrm{m}^\mathrm{BS}(\eta) - Z_\mathrm{m}^\mathrm{SYH}(\eta) \lesssim 0.05$ in the simulated cases. It should be noted however that Eq. (10) tends to overestimate the actual difference $Z_\mathrm{m}^\mathrm{BS}(\eta) - Z_\mathrm{m}^\mathrm{SYH}(\eta)$ (for instance, in the case where $x_1 = 0.25$, $\alpha = 1/3$, $\eta = 0.6$ and $Z_s(\eta)$ is given by Woodcock's EOS, this difference is 0.05, while the prediction of Eq. (10) yields 0.07), so that its main purpose is to illustrate the fact that both EOS yield practically equivalent results for not very asymmetric mixtures. On the other hand, more important differences can be expected for disparate mixtures, especially in the case of large densities. At a given density and a given diameter ratio $\alpha \le 1$ the smallest value of the parameter ξ corresponds to a mole fraction $x_1 = \alpha/(1+\alpha)$ for the large disks, namely $\xi = 4\alpha/(1+\alpha)^2$. Thus, $\xi \ll 1$ if $\alpha \ll 1$ and, according to Eq. (10), $Z_\mathrm{m}^\mathrm{BS}(\eta) - Z_\mathrm{m}^\mathrm{SYH}(\eta) \simeq \Delta(\eta)$.

Let us consider now the limit in which the small disks become point particles ($\alpha \to 0$) and occupy a negligible fraction of the total area. In that case, the compressibility factor of the mixture must reduce to [3, 13]

$$Z_\mathrm{m}(\eta) \to \frac{x_2}{1-\eta} + x_1 Z_\mathrm{s}(\eta). \tag{12}$$

The first term represents the (ideal gas) partial pressure due to the point particles in the available area (i.e., the total area minus the area occupied by the large disks), while the second term represents the partial pressure associated with the large disks. In the limit $\alpha \to 0$ with x_1 finite (or, more generally, for $\alpha \ll x_1$), we have $\xi \to x_1$ and $\beta \to (1 - b_3/2)x_2/(1 + x_1)$ [note that in this limit the approximation (9) becomes correct], so that

$$Z_\mathrm{m}^\mathrm{SYH}(\eta) \to \frac{x_2}{1-\eta} + x_1 Z_\mathrm{s}(\eta), \tag{13}$$

$$Z_\mathrm{m}^\mathrm{BS}(\eta) \to 1 + \frac{1}{2}\left[1 + x_1 + x_2\left(1 - \frac{b_3}{2}\right)\eta\right]\left[Z_\mathrm{s}(\eta) - 1\right]. \tag{14}$$

Therefore, while Eq. (5) is consistent with the exact property (12), Eq. (1) violates it. In fact, the right-hand side of (10), with $\xi = x_1$, gives the deviation of Barrio and

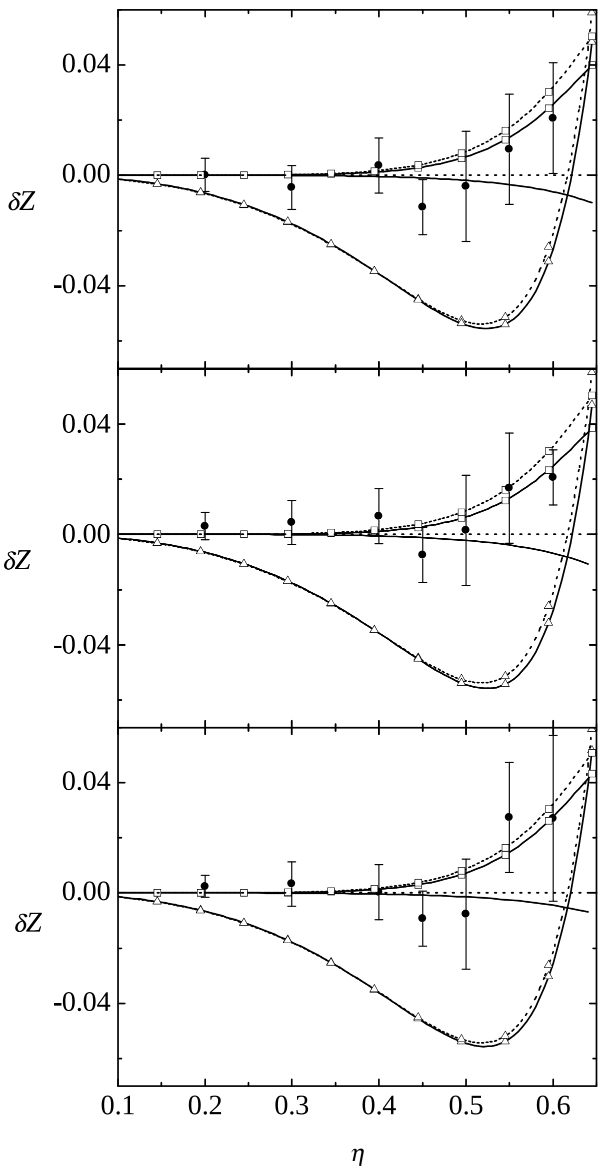

FIG. 1: Plot of the difference $\delta Z(\eta) \equiv Z_{\mathrm{m}}(\eta) - Z_{\mathrm{m}}^{\mathrm{BS(W)}}(\eta)$ for a size ratio $\sigma_2/\sigma_1 = 2/3$ and for $x_1 = 0.25$ (top panel), $x_1 = 0.50$ (middle panel), and $x_1 = 0.75$ (bottom panel). The filled circles are Monte Carlo data [5], the dashed lines refer to the proposal (1), and the solid lines refer to the proposal (5). The EOS of the single component fluid, $Z_{\mathrm{s}}(\eta)$, used as input are Eq. (6) (lines without symbols), Eq. (7) (lines with squares), and Eq. (8) (lines with triangles).

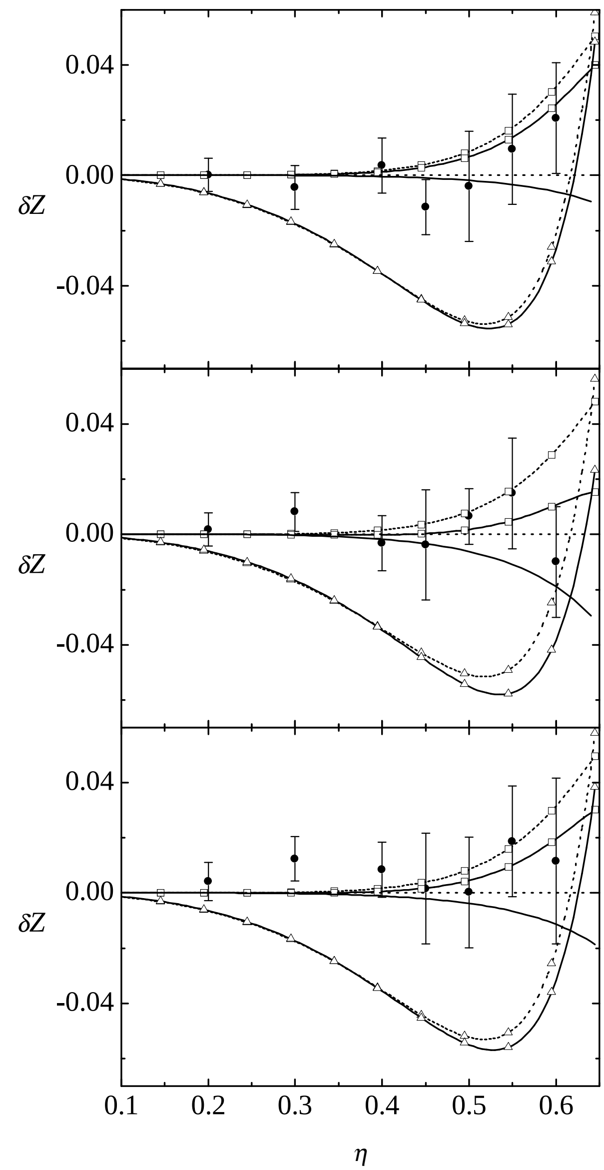

FIG. 2: Same as in Fig. 1, but for a size ratio $\sigma_2/\sigma_1 = 1/2$.

Solana's EOS from the exact compressibility factor in the special case $\alpha \to 0$.

In summary, in this report we have performed a detailed comparison of the EOS proposed by Barrio and Solana [5] and the one introduced by Santos *et al.* [3]. We find that both proposals lead to comparable accuracy when the same EOS for the single component system is used and confirm that the more accurate the $Z_{\mathrm{s}}(\eta)$ the more accurate the resulting compressibility factor for the binary mixture. In favor of Santos *et al.*'s proposal, apart from its simpler form which also yields a very reasonable estimate of the known third virial coefficient, is the fact that it is readily extendible to the multicomponent case (including polydisperse mixtures) and complies with the exact limit in which the small disks are point particles, while $Z_{\mathrm{m}}^{\mathrm{BS}}(\eta)$ does not share these assets.

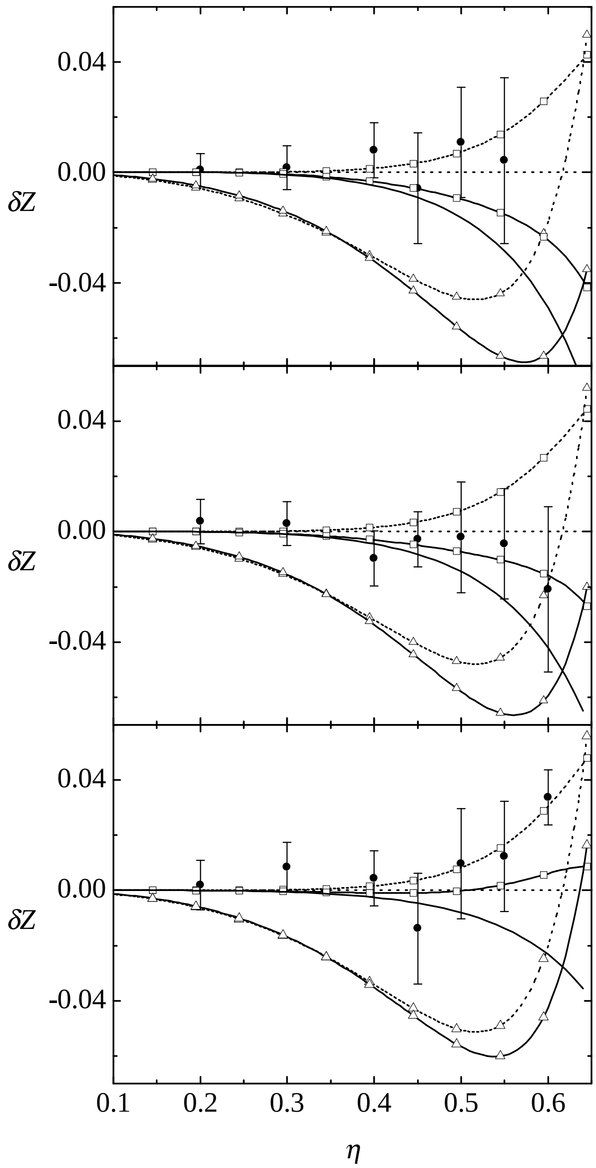

FIG. 3: Same as in Fig. 1, but for a size ratio $\sigma_2/\sigma_1 = 1/3$.

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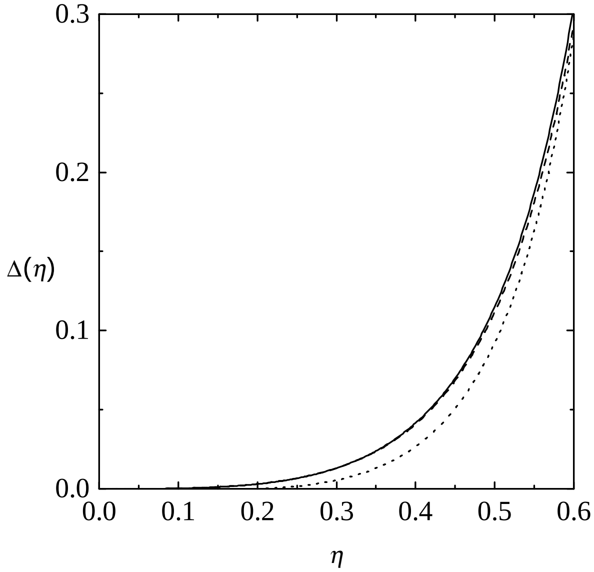

FIG. 4: Plot of $\Delta(\eta)$, Eq. (11), by assuming Woodcock's EOS (dashed line), the Levin approximant (solid line), and the SHY EOS (dotted line) for the pure fluid.